ORGANOMETALLICS

Development of Ferrocene-Based Planar Chiral Imidazopyridinium Salts for Catalysis

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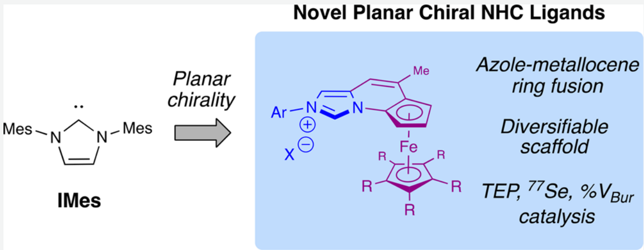
ABSTRACT: Imidazol-2-ylidenes and their N,N′-diaryl derivatives constitute an important class of N-heterocyclic carbenes (NHCs) which possess a unique level of versatility in both organocatalysis and transition-metal catalysis. However, there remain few examples of carbenes of this type that are chiral. Here we describe the development of a family of closely related imidazopyridine-based NHCs that derive their asymmetry purely from planar chirality through the incorporation of the classic metallocene framework. An NMR analysis of ^{77}Se complexes of this family is used to assess their degrees of σ donicity and π acidity in comparison to a larger family of NHCs. Percent buried volume (%V_{bur}) calculations were performed to measure the steric bulk of this distinct class of NHCs. Additionally, these NHCs were employed in various enantioselective transformations to survey their use as organocatalysts as well as ligands for transition-metal-catalyzed processes.



The efficient synthesis of enantiopure substances is a crucial enterprise for the production of pharmaceuticals, agrochemicals, and other fine chemicals. However, the continued expansion of the asymmetric chemical space available to chemists undoubtedly relies upon the construction of new catalyst architectures. Toward this end, established achiral catalyst motifs can serve as highly effective templates for new chiral scaffolds, provided that their integration in a chiral framework does not compromise their original reactivity, stability, and synthetic accessibility.

Since the development of 1,3-bis(2,4,6-trimethylphenyl)-imidazole-2-ylidene (IMes) by Arduengo in 1992,[1] this archetype imidazolium scaffold has enjoyed extensive use as a ligand in transition-metal catalysis[2] as well as a suitable organocatalyst.[3] Given this marked versatility, successful implementations of this archetype within a chiral framework have the potential to be strongly effective in diverse areas of chemical methodology. Nevertheless, key features of IMes, including its plane of symmetry and lack of sp^3-hybridized atoms in the core heterocycle, impede its straightforward invocation of chirality. Thus, examples of *chiral* carbenes that retain the defining aromatic framework of IMes remain comparatively scarce.

One approach to attain chirality without the need for sp^3-hybridized carbon centers is through the incorporation of hindered aromatic systems, preventing free rotation and thus imparting chirality in the structure. Early examples of NHCs containing this type of axial chirality include the bis-imidazolium developed by Rajanbabu[4] and Hoyveda's[5] olefin metathesis catalyst (Figure 1A). In these examples, the 1,1-binaphthyl moiety is the source of chirality, as the bulky substituents attached prevent rotation around the bridging carbon−carbon bond.

Related to these concepts, a special case of axial chirality, termed planar chirality, arises from two dissymmetric rings fixed in a noncoplanar, yet parallel, orientation.[6] The most common examples of planar chirality feature the classic metallocene motif, which consists of a metal center in complexation with two η^5-cyclopentadienyl (Cp) rings. While there have been numerous descriptions of planar chiral phosphine ligands,[7] the number of NHC ligands incorporating this design is limited.[8] It was not until 2002 that Bolm and co-workers introduced the first planar chiral carbene (Figure 1B).[9] This was shortly followed by reports of similar ligands including Togni's bisferrocenyl NHC[10] and Seimeling's[11] redox-active carbene. These few examples exemplify the need for new planar chiral derived NHCs, especially those that do not feature free rotation of the ferrocenyl motif relative to the plane of the NHC, allowing for a more rigid structure.[12]

With the aim of enriching the pool of chiral IMes-equivalent carbenes through a metallocene-based design, we recently disclosed a new class of planar chiral ferrocenyl IMes-type

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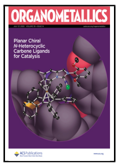

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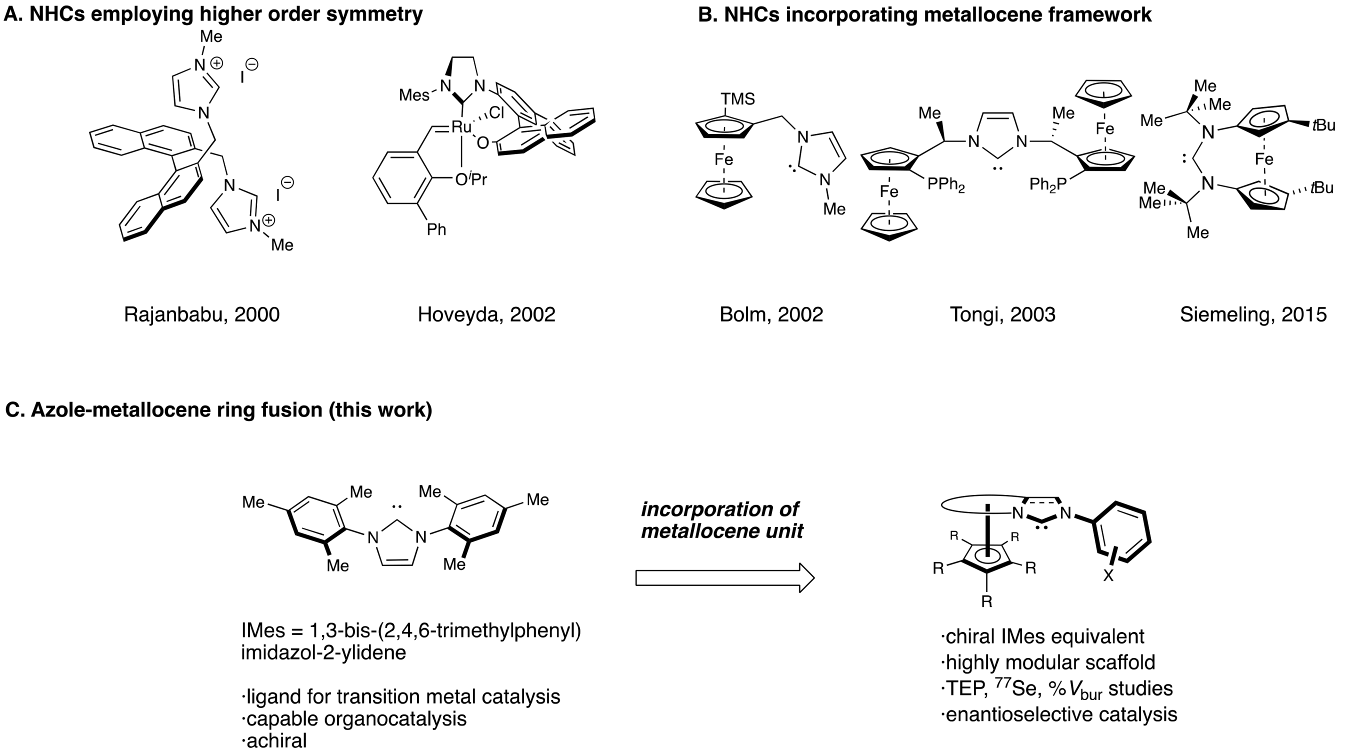

Figure 1. Examples of NHCs invoking higher order symmetry.

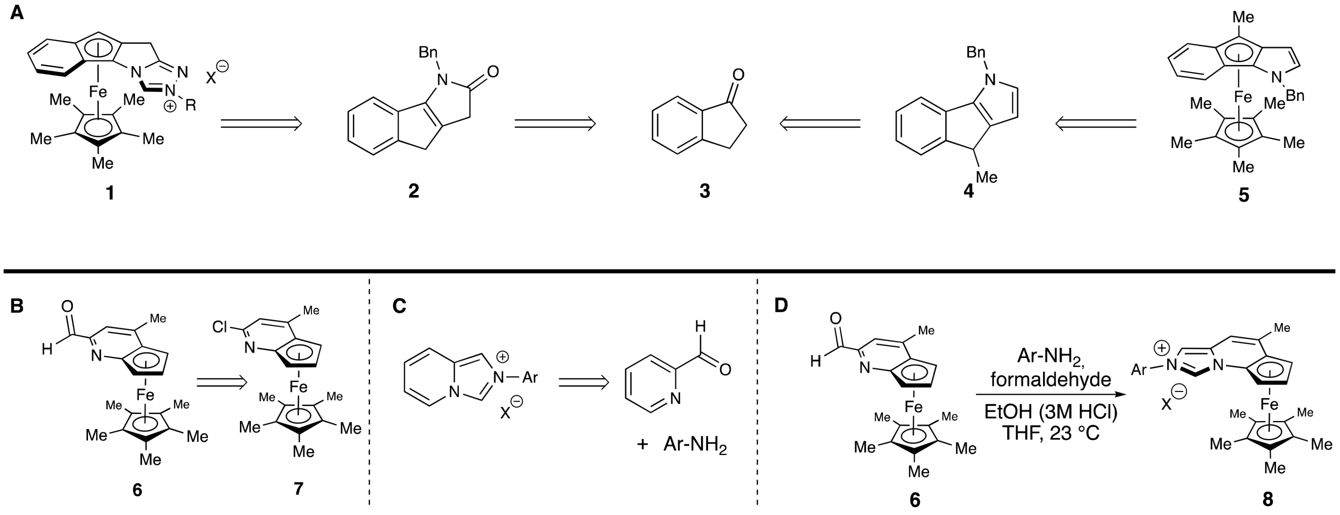

Figure 2. Original retrosynthetic analysis (A). New retrosynthetic approaches (B, C). Proposed key annulation step (D).

NHCs which were demonstrated to be highly selective in several Cu(I), Ni(0), and free carbene catalyzed processes.[13] In this report, we focus on (i) our initial efforts toward construction of a planar chiral azolium salt and the ensuing evolution of our primary designs, (ii) an expanded account of the metal complexes synthesized with our platform including more robust characterization and analysis, and (iii) recent developments in using these NHCs in enantioselective transformations (Figure 1C).

Initial efforts toward achieving a viable synthesis of a ligand that would meet these criteria focused upon the construction of the rigid 6.5.5.5 scaffold **1** (Figure 2A). It was hypothesized that lactam **2** could be synthesized from the commercially available 1-indanone (**3**). Lactam **2** would then allow a straightforward synthesis to the triazolium. Unfortunately, lactam **2** proved to be difficult to make due to its instability, presumably from high ring strain. To circumvent this presumed instability issue, pyrrole **4** was targeted as an intermediate for the synthesis of ferrocene **5**. While pyrrole **4** could be accessed in four steps from **3**, the formation of **5** proved to be quite challenging. Ferrocene **5** was observed via LCMS; however, all attempts to isolate it were unsuccessful, as **5** readily decomposed on exposure to air and silica gel.

After further investigation of the literature, two key reports from the laboratories of Fu[14] and Aron[15] (Figure 2B,C, respectively) provided inspiration for the third-generation synthesis of our planar chiral NHCs. We believed that, by accessing the well-established ferrocenyl chloropyridine intermediate **7** described by Fu and co-workers, we could synthesize the desired aldehyde **6** through a palladium-

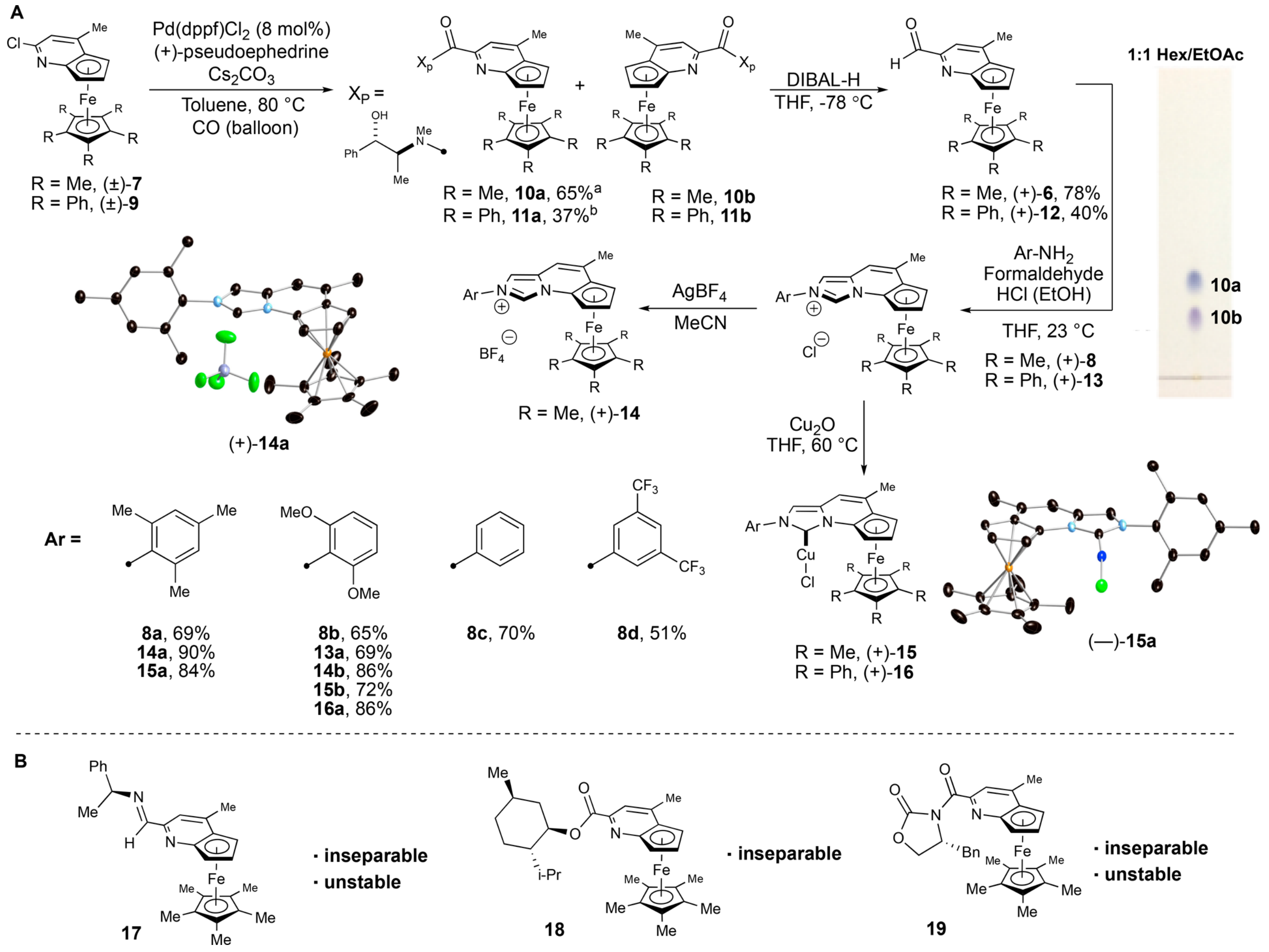

Figure 3. Synthesis of planar chiral imidazolium salts (A). (a, b) combined yields. Chiral auxiliaries screened for diastereomeric separation (B).

catalyzed carbonylation reaction.[16] With the ferrocenyl aldehyde in hand, we could employ the annulation conditions discovered by Hutt and Aron to provide planar chiral NHCs **8** (Figure 2D).

Racemic ferrocenyl chloropyridine (±)-**7** can be synthesized in six steps on a multigram scale and proved to be a useful intermediate for our synthesis route (Figure 3A). Originally, the enantiopure aldehyde (+)-**6** was attained by chiral preparative HPLC; however, we felt that a more general method should be developed for large-scale synthesis and ease of access. This caused us to examine different chiral auxiliaries, which would allow for the diastereomers to be separated via column chromatography or recrystallization (Figure 3B). Products **17**–**19** were all observed by LCMS; however, none of the resulting diastereomers could be separated and most were unstable toward silica gel. To our delight, it was found that pseudophedrine could be used as the auxiliary in a direct palladium-catalyzed aminocarbonylation reaction with (±)-**7**, to provide a mixture of diastereomers (**10a** and **10b**). The mixture of **10a** and **10b** could be separated by flash column chromatography in a 1/1 mixture of hexanes and ethyl acetate. Both products were also easily identifiable by TLC. The pseudoephedrine auxiliary was then removed through reduction with DIBAL-H to yield the corresponding enantiopure aldehyde (+)-**6**. Finally, the formation of the planar chiral imidazolium core (+)-**8** was attained through the annulation reaction presented by Hutt and Aron with slightly modified conditions (Figure 1A). The hydrochloride salts allowed for anion exchange with AgBF$_4$ to afford the tetrafluoroborate salts **14** or for copper complex formation (**15** and **16**) with Cu$_2$O. Gratifyingly, this entire process can be also implemented by starting with the pentaphenyl-derived Cp ring intermediate (±)-**9** to afford the sterically encumbered imidazolium salt (+)-**13**.

The annulation step in synthesizing the azolium core was crucial, as it allowed for late-stage diversification. However, our original report only focused on using simple anilines without an additional Lewis basic site such as pyridines and phosphines. It was our goal to expand this new family of NHCs to create a potential bidentate ligand system. Unfortunately, most anilines containing an additional Lewis base functionality were unsuccessful in the annulation of aldehyde **6** except for thioanisole **8e** and phenol **8f** (Scheme 1). It should be noted that the conditions established by Berthon-Gelloz[17] were required for the synthesis of these new azoliums. Given that Aron's simpler substrates showed a broad tolerance to polyamines, anilines, and alcohols, we can attribute this discrepancy to either diminished solubility or electronic factors related to the increased nucleophilicty of our ferrocenyl aldehyde **6**.

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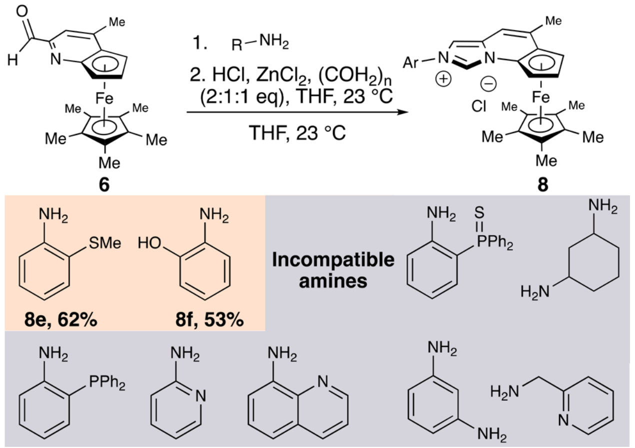
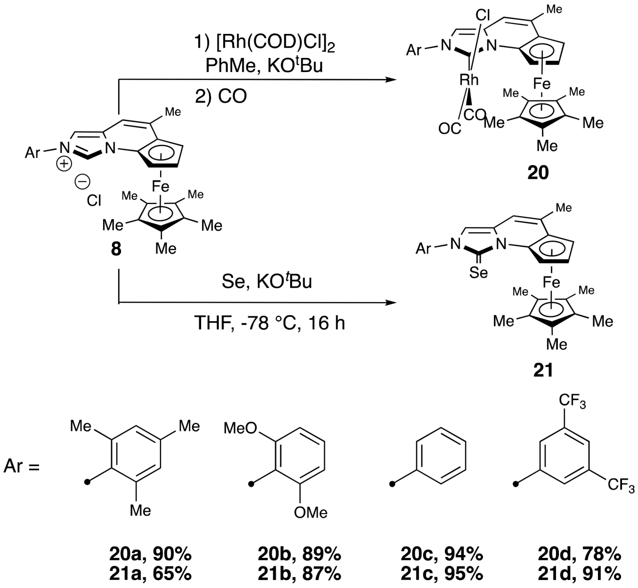
Scheme 1. Attempted Anilines for a Bidentate Ligand System



To further our understanding of this new class of NHCs, several rhodium(I) carbonyl complexes and selenium adducts were prepared (Scheme 2).

Scheme 2. Synthesis of Rh(I) and Se Complexes

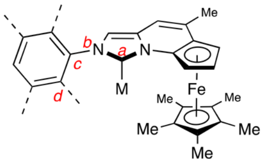


In our initial analysis of the electronic properties of this ligand class, we relied upon the Tolman electronic parameter (TEP), a widely utilized metric for the degree to which a NHC ligand influences electron density on the metal center.[18] While NHCs have traditionally been regarded as purely σ donor ligands, there has been experimental and theoretical evidence that π back-donation may have a significant effect on the metal−carbene bond.[19] It is now understood that these TEP studies can only measure the net effect of π acidity and σ donicity between an NHC and its metal center. To address these concerns, Bertrand disclosed a ^{31}P NMR based methodology, which allows for accurate assessment of the NHC π acidity.[20] Likewise, Ganter described an analogous method studying ^{77}Se-NHC complexes.[19,21]

In our application of these methods, it was found that **20a** had a TEP comparable to that of IMes (Table 1). These results were exciting, as the original goal was to create a chiral IMes equivalent that could be employed in catalysis. While **20b** contained the largest TEP in comparison to **20a**, both **21a** and **21b** had similar ^{77}Se chemical shifts. Despite their similar degrees of π acidity, NHC **8b** maintains a higher degree of σ donicity leading to a higher level of electron density on the metal center.

Table 1. Spectroscopic Data of Rh(I) and Se Complexes with Selected Literature Examples

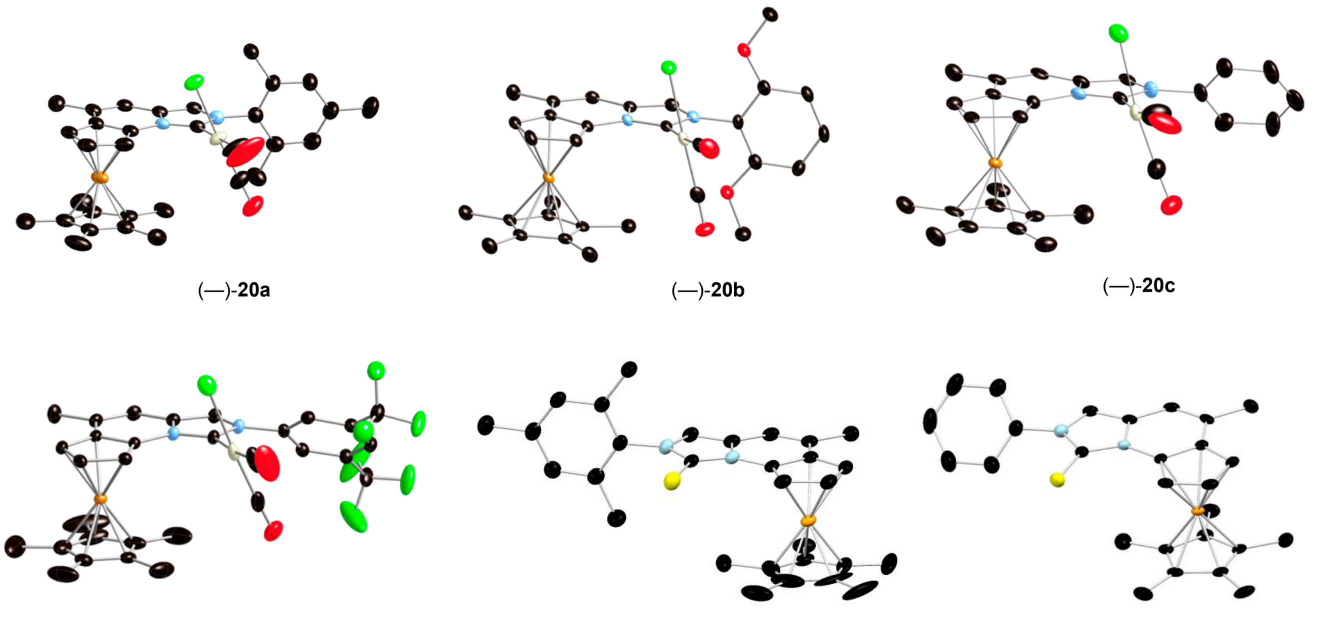
NHC	NHC-Rh(CO$_2$)Cl (**20**) TEP (cm^{-1}) a-b-c-d torsion (°)[a]	NHC-Se (**21**) δ ^{77}Se (ppm)[b,c]
a	2049 82	94
b	2047 96	100
c	2050 49	112
d	2054 61	117
SIMes	2052 -	116
IMes	2050 -	35



[a] See the structure at the bottom of the table for atom labels. [b] ^{77}Se chemical shift of selenium bound to the carbine carbon. [c] Taken in acetone-d_6.

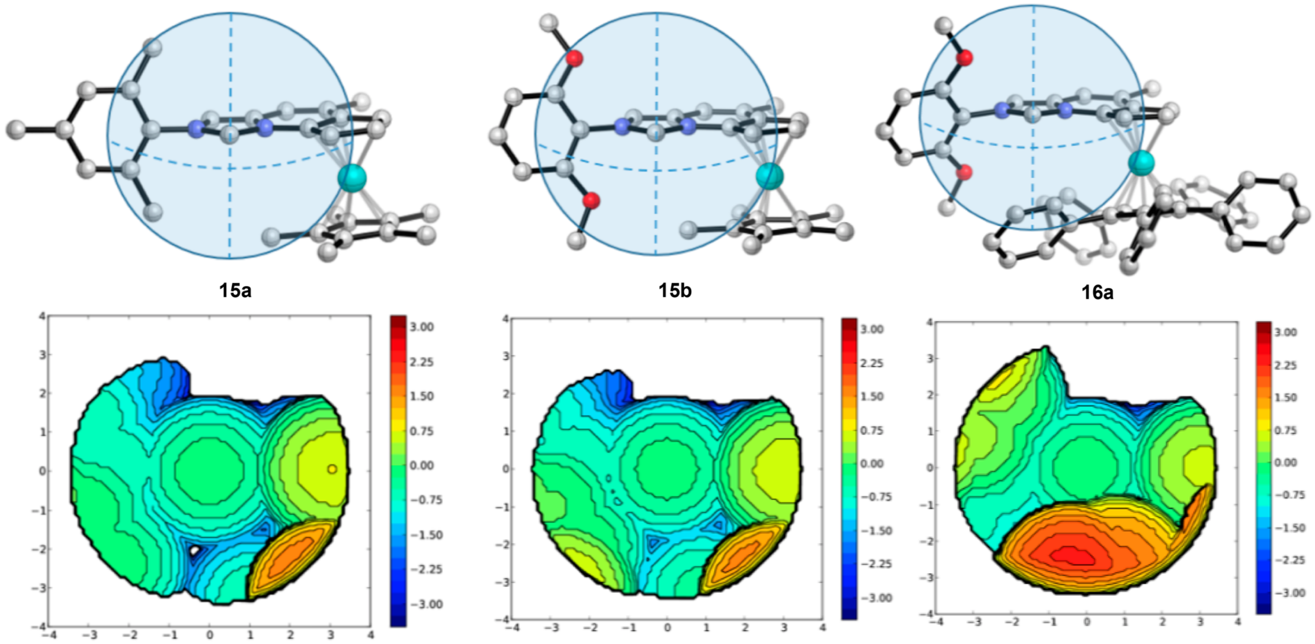
We note that while **20c** and **20d** exhibit contrasting TEP values relative to one another, **21c** and **21d** are quite similar in their ^{77}Se chemical shifts, which greatly contrast with those of **21a** and **21b**. This relative clustering of NHCs **a**/**b** vs NHCs **c**/**d** can presumably be attributed to the ability of the wingtip aryl group to rotate and undergo conjugation with the polycycle. For example, in the crystal structures of (−)-**20a** and (−)-**20b** (Figure 4), we can see that the aryl group is orthogonal to the azole polycycle due to the large substituents on the ring in comparison to (−)-**20c** and (+)-**20d**, where the aryl rings are much more in plane with the azole core. The aryl groups on (−)-**20a** and (−)-**20b** prevent rotation, thus constraining the molecule and suppressing π delocalization.

As a class, the overall placement of **a**−**d** among a broader context of NHCs on the ^{77}Se scale reveals similarities to SIMes. While the TEP of IMes is comparable to those of **a** and **c**, its ^{77}Se shift implies a substantially diminished degree of π acidity and thus a much smaller magnitude of σ donicity in comparison to **a**−**d**. While TEP and ^{77}Se shifts are not directly correlated, this large discrepancy suggests that π acidity may


(−)-**20a** (−)-**20b** (−)-**20c**

(−)-**20d** (+)-**21a** (+)-**21c**

Figure 4. X-ray structures of Rh(I) and ^{77}Se complexes. Hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability. The Rh(I) complexes were derived from the diastereomer **10b**.


15a **15b** **16a**

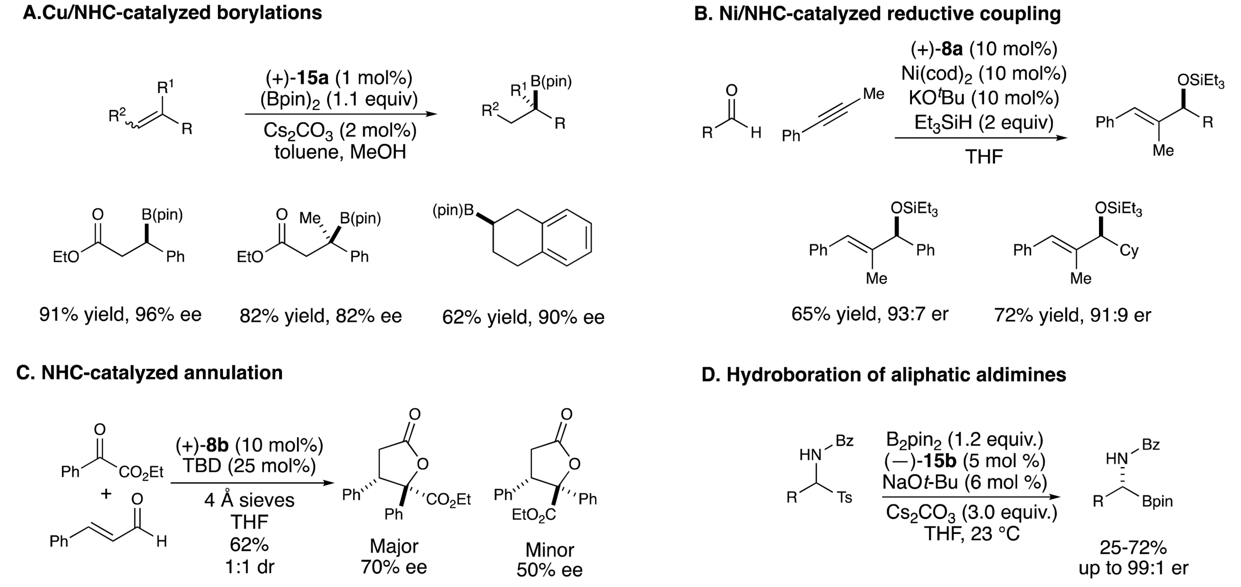
NHC	%V_{Bur} Total	NE	SE	SW	NW
15a	38.7	33.3	51.5	39.5	30.7
15b	39.5	33.2	51.5	45.3	28.0
16a	51.3	31.9	68.8	58.2	46.3

Figure 5. %V_{Bur} and corresponding heat maps. Blue-shaded areas represent a 7.0 Å diameter spherical volume centered 2.0 Å from the carbene carbon. Axes and legend units are given in angstroms. See the Supporting Information for details.

serve as a more important factor in modulating the net electron donicity of our ligands.

Following our interest in understanding the electronic properties of these NHCs, we additionally wanted to examine the influence of steric factors provided by this new ligand class. Whereas cone angles are typically used to understand the steric properties of phosphine ligands, buried volume (%V_{Bur}) calculations are an alternative method that allow us to assess the overall steric encumbrance around a hypothetical metal center for a set of ligands, especially for NHC ligands.[22] %V_{Bur}

Scheme 3. Various Transformations Using Planar Chiral NHCs



analysis includes a quantitative assessment of occupancy in each generated quadrant. These data can provide insight into a ligand's ability to project an asymmetric environment around its key reactive space.

Several copper(I) complexes were synthesized, and $\%V_{\mathrm{Bur}}$ values revealed that functionalization of the pendant Cp ring unsurprisingly has the greatest effect on total buried volume (Figure 5). The pentaphenyl derivative **16a** contained the largest $\%V_{\mathrm{Bur}}$ occupancy with 51.3% of its simulated coordination sphere being occupied. This value is extremely high in comparison to other Arduengo-type NHCs, which typically range from 20 to 35% $\%V_{\mathrm{Bur}}$.[22b] This large $\%V_{\mathrm{Bur}}$ of **16a** is approached by Bertrand's CAAC-type ligand (51.2% $\%V_{\mathrm{Bur}}$)[23] and Glorius' (−)-menthone-derived IBiox NHC (47.8% $\%V_{\mathrm{Bur}}$)[24] and more recently surpassed by Rivard's trityl-derived NHCs (57.3% $\%V_{\mathrm{Bur}}$).[25] All examined complexes showed a high occupancy in the southeast (SE) quadrant where the bulky Cp ring is located. Altering the wingtip aryl position had a minimal effect on the total $\%V_{\mathrm{Bur}}$ on comparison of **15a** and **15b**; however, we note that the northwest (NW) quadrant of **16a** is still highly occupied despite containing the same aryl group as **15b**. This can be attributed to possible repulsion of the Cp ring and methoxy substituents. The large disparity between the $\%V_{\mathrm{Bur}}$ values of these complexes demonstrates the potential tunability of these ligands through modification of the Cp base or more complex N-aryl substituents.

With an established route to new planar chiral imidazolium salts and metal complexes in hand, we were eager to apply these catalysts in a variety of reactions to probe their reactivity and ability to induce enantioselectivity (Scheme 3). We were able to use Cu(I) catalyst (+)-**15a** in various borylation reactions to afford the borylated products in good yields and selectivities without the need for optimization (Scheme 3A).[26] Catalyst (+)-**8a** was successful when it was used as a ligand in nickel-catalyzed reductive coupling reactions (Scheme 3B).[27] NHC (+)-**8b** was found to be a suitable Lewis base catalyst in the homoenolate addition of cinnemaldehyde to α-keto esters (Scheme 3C).[28] Finally, we successfully reported the first highly enantioselective hydroboration of aliphatic aldimines using the Cu(I) complex (−)-**15b** (Scheme 3D).[29]

In summary, this work provides a successful strategy for the synthesis of a new family of chiral NHC ligands that fuse together a metallocene framework with an imidazolium-like core. These azolium salts and subsequent NHCs allow for simple modification either through altering the Cp ring or through late-stage diversification of the N-aryl wingtip. These modifications greatly affect the steric and electronic properties of these NHCs as shown by TEP studies, ^{77}Se NMR spectroscopy analysis, and buried volume calculations. While these NHCs have been successful and selective in various transformations, the ongoing challenge now lies within further extending the current scope to additional metallocene cores and chelating auxiliary functionalities to provide new reactivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00312.

> Experimental procedures and spectral data for new compounds (PDF)

Accession Codes

CCDC 1999565 and 1999567 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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